

Environmental Chamber Studies of Ozone Formation Potentials of Volatile Organic Compounds

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Key Words

Environmental chambers, Atmospheric chemical mechanisms, Ozone, Aromatic Hydrocarbons, Petroleum Distillates, Coatings VOCs; SAPRC-99 Mechanism

Abstract

Selected results of environmental chamber experiments carried out in the new large indoor environmental chamber at the University of California at Riverside (UCR) that are relevant to quantifying ozone impacts of volatile organic compounds (VOCs) are described. Issues and data needs for quantification of VOC reactivities towards ground-level ozone are described. The ability of the current SAPRC-99 chemical mechanism to simulate recent data from this chamber concerning the ozone formation from irradiations of an ambient reactive organic gas (ROG) - NO_x mixture and several new aromatics experiments are discussed. It was found that the mechanism consistently underpredicts ozone formation in ambient surrogate - NO_x experiments at low ROG/NO_x ratios, and also underpredicts the effects of adding CO to aromatic - NO_x irradiations. The two problems may be related and suggest problems with the formulation of current mechanisms for atmospheric reactions of aromatics.

Background

Many different types of volatile organic compounds (VOCs) are emitted into the atmosphere, where they can affect photochemical ozone formation and other measures of air quality. Because they can react in the atmospheres at different rates and with different mechanisms, the different types of VOCs can vary significantly in their effects on air quality. The effect of a VOC on ozone formation in a particular environment can be measured by its "incremental reactivity", which is defined as the amount of additional ozone formed when a small amount of the VOC is added to the environment, divided by the amount added. Although this can be measured in environmental chamber experiments, incremental reactivities in such experiment cannot be assumed to be the same as incremental reactivities in the atmosphere (Carter and Atkinson, 1989; Carter et al., 1995). This is because it is not currently practical to duplicate in an experiment all the environmental factors that affect relative reactivities; and, even if it were, the results would only be applicable to a single type of environment. The only practical means to assess atmospheric reactivity, and how it varies among different environments, is to estimate its atmospheric ozone impacts using airshed models.

However, airshed model calculations are no more reliable than the chemical mechanisms upon which they are based. While the initial atmospheric reaction rates for most VOCs are reasonably well known or at least can be estimated, for most VOCs the subsequent reactions of the radicals formed are complex and have uncertainties that can significantly affect predictions of atmospheric impacts. For this reason, environmental chamber experiments and other

experimental measurements of reactivity are necessary to test and verify the predictive capabilities of the chemical mechanisms used to calculate atmospheric reactivities.

As discussed in a companion paper (Carter, 2004a), under U.S. EPA funding the “UCR EPA” chamber has been constructed at the University of California at Riverside (UCR) in order to address some of the deficiencies of environmental chambers previously used for mechanism evaluation. This chamber has been generating mechanism evaluation data since early 2003, both for general ozone formation mechanism evaluation, and for evaluation of ozone impacts of selected coatings VOCs. The data have been used to evaluate the SAPRC-99 gas-phase mechanism (Carter, 2000), which, together with the European Master Chemical Mechanism (MCM) (Jenkin et al, 1997; Saunders et al, 2003; Jenkin et al, 2003; MCM 2004) represents one of the two state-of-the-art mechanisms that can be used to assess ozone impacts of many individual VOCs. Although the evaluation of the MCM against chamber data is currently underway (e.g., Pilling, 2004; Pinho et al, 2003), SAPRC-99 is still the most extensively evaluated of the mechanisms against available chamber data (Carter, 2000).

In this paper, we will discuss the results of the evaluations of the SAPRC-99 mechanism with UCR EPA chamber data relevant to chemical mechanism uncertainty with respect to predictions of effects of VOCs on ozone. The data discussed here are relevant “base mechanism” uncertainty, which refer to general uncertainties in the predictions of ozone formation from reactive organic gas (ROG) and NO_x mixtures representing ambient pollution. This is important to prediction of effects of overall VOC and NO_x controls and also to appropriately representing the chemistry of base case conditions when assessing incremental reactivities of various types of individual types of VOCs. The specific experiments discussed here are ambient ROG surrogate - NO_x experiments at varying ROG and NO_x levels, and experiments to evaluate the photooxidation mechanism for aromatics, which are important and highly reactive components of the ambient ROG mixture.

Prediction of Ozone formation in Ambient ROG Surrogate - NO_x Experiments

As discussed in our companion presentation (Carter, 2004a), the initial experiments carried out in the UCR EPA chamber consisted of a large number of ambient ROG surrogate - NO_x experiments carried out at varying initial NO_x and ROG levels. The ambient ROG surrogate composition was derived as discussed by Carter et al (1995) and consisted of a simplified mixture of designed to represent the major classes of hydrocarbons and aldehydes measured in ambient urban atmospheres, with one compound used to represent each model species used in current condensed lumped-molecule mechanisms. The eight representative compounds used were n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene, and formaldehyde. The initial NO_x levels varied from 2 to ~300 ppb and the initial ROG levels varied from ~0.2 to 4.2 ppmC.

Figure 1 shows the matrix of initial ROG and NO_x levels of the ambient ROG surrogate - NO_x experiments carried out in the UCR EPA chamber for mechanism evaluation. The different symbols indicate the project for which the experiment was conducted and whether radical measurement data were made, but for the purpose of this discussion they all are the same experiment except for the varying ROG and NO_x levels. Note that this is a log-log plot, with the initial NO_x varying by almost two orders of magnitude, and the initial ROG varying by over one

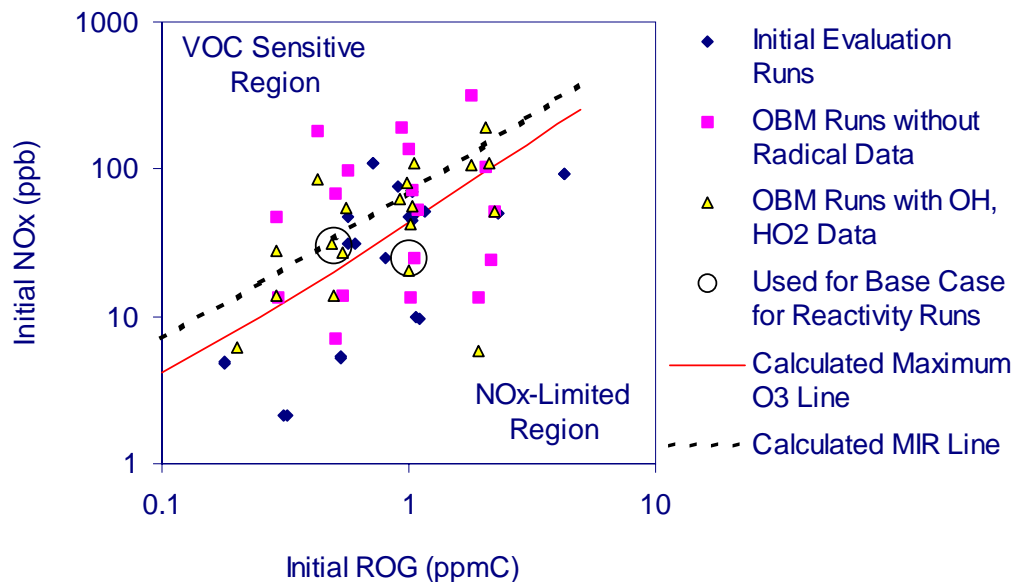


Figure 1. Matrix of initial ROG and NO_x levels in the ambient ROG surrogate - NO_x experiments carried out in the UCR EPA chamber. The initial ROG and NO_x levels used in the base case experiments for the incremental reactivity studies of the coatings VOC emissions are also shown.

order of magnitude. The solid line show the ROG/NO_x levels that the SAPRC-99 mechanism predicts give the highest ozone levels and the dotted line shows the ROG/NO_x levels where the mechanism predicts O₃ has the greatest sensitive to changes in VOC levels (MIR line). It can be seen that the matrix includes experiments in both the VOC sensitive and NO_x-sensitive regions as defined by these lines.

The two large open circles on Figure 1 show the ROG and NO_x levels chosen to serve as the “base case” in the incremental reactivity experiments that are currently underway in this chamber to assess ozone impacts of various different types of VOCs (Carter, 2004c). The 25-30 ppb NO_x levels were chosen to be representative of pollution episodes of interest in California, based on input provided by the staff of the California Air Resources Board, which is funding most of the current reactivity studies. The ROG/NO_x ratios were chosen to represent two sets of conditions of NO_x availability relevant to VOC reactivity. The lower ROG/NO_x ratio was chosen to represent the relatively higher NO_x conditions of maximum incremental reactivity (MIR) where ozone is most sensitive to VOCs, to approximate the conditions used to derive the widely-used MIR ozone reactivity scale (Carter, 1994). The higher ROG/NO_x ratio was chosen to be one-half that yielding maximum ozone levels, and is used to represent conditions where ozone is NO_x-limited, but not so NO_x-limited that VOC reactivity is irrelevant. These are referred to in the subsequent discussion as the “MIR” and “MOIR/2” base cases, respectively.

The ability of the SAPRC-99 mechanism to simulate ozone formation in representative MIR and MOIR/2 base case experiments is shown on Figure 2. It can be seen that good

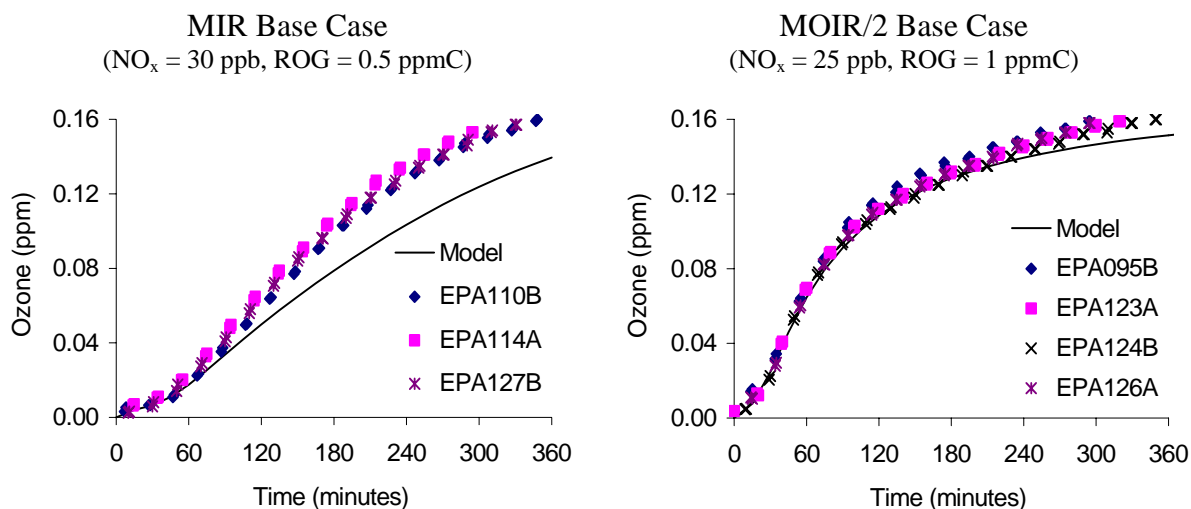


Figure 2. Experimental and calculated concentration-time plots for ozone in representative base case experiments used for VOC reactivity assessment.

reproducibility in ozone formation is observed in the replicate experiments, but that the model consistently underpredicts O_3 formation in the MIR experiments, though it gives much better predictions of ozone in the experiment at the higher ROG/ NO_x ratio. This tendency to underpredict O_3 in the base case experiment representing MIR conditions presents a problem when using incremental reactivity MIR experiments for evaluating mechanism of added VOCs.

The dependence of the tendency for the SAPRC-99 mechanism underprediction bias on the initial ROG/ NO_x ratio is shown on Figure 3. In order to provide useful mechanism evaluations at the lowest ROG/ NO_x ratios where O_3 formation is suppressed by NO, the model predictions of ozone formed + NO oxidized, measured by $([O_3]_{final} - [NO]_{final}) - ([O_3]_{initial} - [NO]_{initial})$ or $\Delta([O_3] - [NO])$, is shown. Comparable results of a recent SAPRC-99 mechanism evaluation using ambient surrogate - NO_x data from other low NO_x environmental chamber datasets (Carter, 2004b, and references therein) are also shown. In order to place the ROG/ NO_x ratios for the various chamber datasets on the same basis, the biases are plotted against ROG/ NO_x ratios normalized to the ratio calculated to give the highest ozone formations for the conditions of the various chambers.

Although this was not evident from the previous mechanism evaluation using higher NO_x chamber data with higher chamber effects (Carter, 2000; see also Carter, 2004b), the results of this work show a consistent tendency of increase in ozone underprediction bias with decreasing ROG/ NO_x ratios for the ambient surrogate experiments in the UCR EPA chamber. This bias may also be present in the simulations of the ambient surrogate experiments in the TVA chamber, which were also carried out at relatively low NO_x levels (Simonaitis and Bailey, 1995; Bailey et al, 1996; Carter, 2004b). The SAPRC-99 mechanism underpredicts O_3 formation and NO oxidation in almost all the ambient surrogate experiments carried out in the Australian CSIRO chamber that were used for low NO_x mechanism evaluation (Hess et al, 1992; Johnson et al, 1997; Carter, 2004b). Although this might be due to characterization uncertainties with this

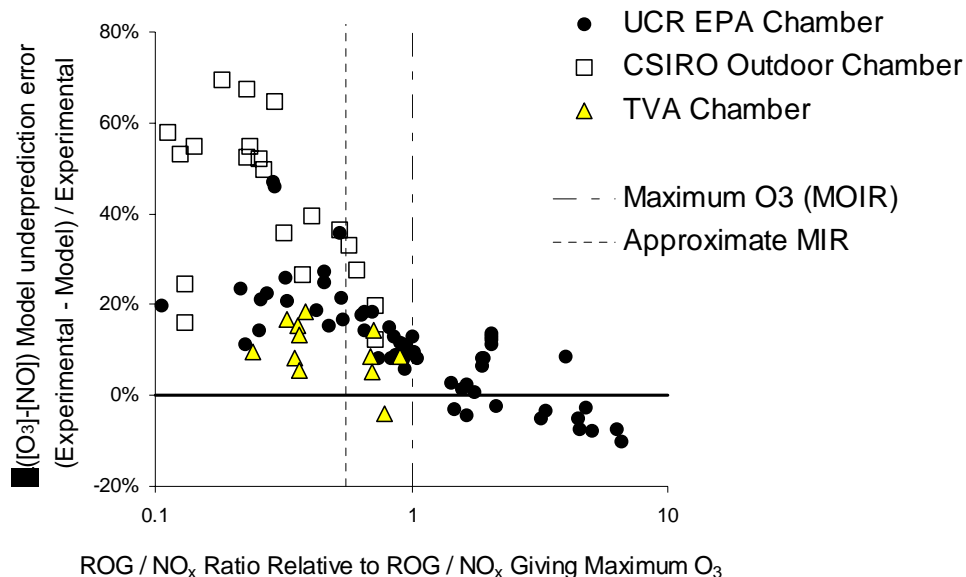


Figure 3. Plots of the bias for the SAPRC-99 mechanism to underpredict NO oxidation and O₃ formation against normalized ROG/NO_x ratios for ambient surrogate - NO_x experiments in three environmental chambers.

outdoor chamber (Carter, 2004b), if the relative ROG/NO_x ratios are taken into account the results are entirely consistent with the trends observed when modeling the UCR EPA experiments.

Figure 4 shows the effects of using different mechanisms or mechanism parameters on plots of the underprediction bias the UCR EPA ambient surrogate experiments. The filled diamonds show the same results as shown on Figure 3 for this chamber, and the error bars show the effects of varying the HONO offgassing chamber effect parameter from zero to the maximum level indicated by the variability of the characterization experiments. This is probably the most important chamber effects parameter that would affect the results of model simulations of these experiments, since the radical source caused by the HONO photolysis will affect the results of the low ROG/NO_x experiments while the NO_x input caused by this process will affect the high ROG/NO_x runs. While this variable chamber effect has a non-negligible effect, it is not enough to explain the underprediction bias observed at the low ROG/NO_x ratios. On the other hand, it could account for the apparent *overprediction* bias at the highest ROG/NO_x ratios.

Various sensitivity studies have indicated that uncertainties in the rate constant for the reaction of OH with NO₂, an important radical termination and NO_x process, could have effects of model simulations of O₃. In order to assess whether this could account for the bias observed, simulations were carried out with the rate constant reduced by ~20%, which is probably reflective of its current uncertainty. It can be seen that this reduces the bias somewhat, but does not eliminate it.

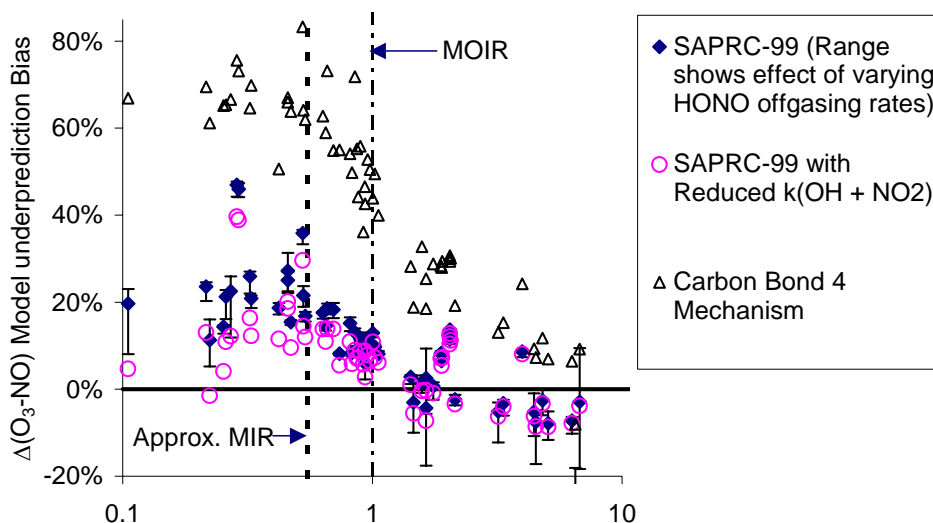


Figure 4. Plots of the mechanism underprediction bias for model simulations UCR EPA ambient surrogate - NO_x experiments against normalized ROG/NO_x ratios for the SAPRC-99 and Carbon Bond mechanisms. The SAPRC-99 calculations show effects of varying the HONO offgasing chamber effect parameters and using a lower $\text{OH} + \text{NO}_2$ rate constant.

Figure 4 also shows that the low ROG/NO_x model underprediction bias is significantly worse for the Carbon Bond 4 mechanism (Gery et al, 1989). Although somewhat out-of-date, this mechanism is still widely used in many models in the United States because of its computational efficiency.

The reason for this underprediction bias is still uncertain, and it is being investigated by conducting experiments with modified ROG surrogates and as part of an ongoing project to update the SAPRC mechanism. We suspect that is probably due to problems with the current mechanism for aromatics, which are highly reactive components of the ambient ROG surrogate whose mechanism remain highly uncertain. Additional evidence for problems with the current aromatics mechanisms is discussed in the following section.

New Aromatics Mechanism Evaluation Results

As discussed in our companion paper (Carter, 2004a), the initial evaluation experiments in the UCR EPA chamber included experiments with the representative aromatic hydrocarbons toluene and m-xylene. Aromatics are important components of ambient ROG mixtures because of their high reactivity, and both toluene and m-xylene are present in the ambient ROG surrogate used in the experiments discussed in the previous section. Aromatics have the most uncertain mechanisms of all the compounds present in this surrogate. Although there have been extensive studies of the atmospheric reactions of aromatics and their reactive products (e.g., see Calvert et al, 2002, and references therein), available information is still insufficient to derive predictive mechanisms. The greatest uncertainty concerns the highly reactive but incompletely

characterized aromatic ring-opening products, whose subsequent reactions appear to be significant radical initiators, since ignoring their reactions results in significant underpredictions of aromatic reactivity. The current SAPRC-99 mechanism and represents the reactions in a highly simplified manner, using a few parameterized model species whose yields and photolysis rates were adjusted to optimize fits of model simulations to aromatic - NO_x chamber experiments (Carter, 2000).

The results of the toluene - NO_x and m-xylene - NO_x experiments in the UCR EPA were reasonably consistent with the predictions of the current SAPRC-99 mechanism, though the mechanism had a slight bias towards overpredicting O₃ in the experiments (see Carter, 2004a for a summary of the fits to total NO oxidation and O₃ formation in the experiments). Examples of experimental and calculated ozone in these runs are shown in Figure 5, where the open squares are the experimental data for representative aromatics - NO_x experiments, and the dotted lines are the model simulations of those runs. A reasonably good fit of the model to these experiments is expected because the parameters in the mechanisms for those compounds were adjusted to optimize model simulations of such experiments. However, the NO_x levels in these experiments were considerably lower than those in the runs used to develop the SAPRC-99 mechanisms, and there was a concern that the parameterization may not extrapolate to lower NO_x levels. Apparently the parameterization employed is no less applicable for NO_x levels as low as ~5 ppb than it is for the higher NO_x levels in the experiments used in the mechanism development.

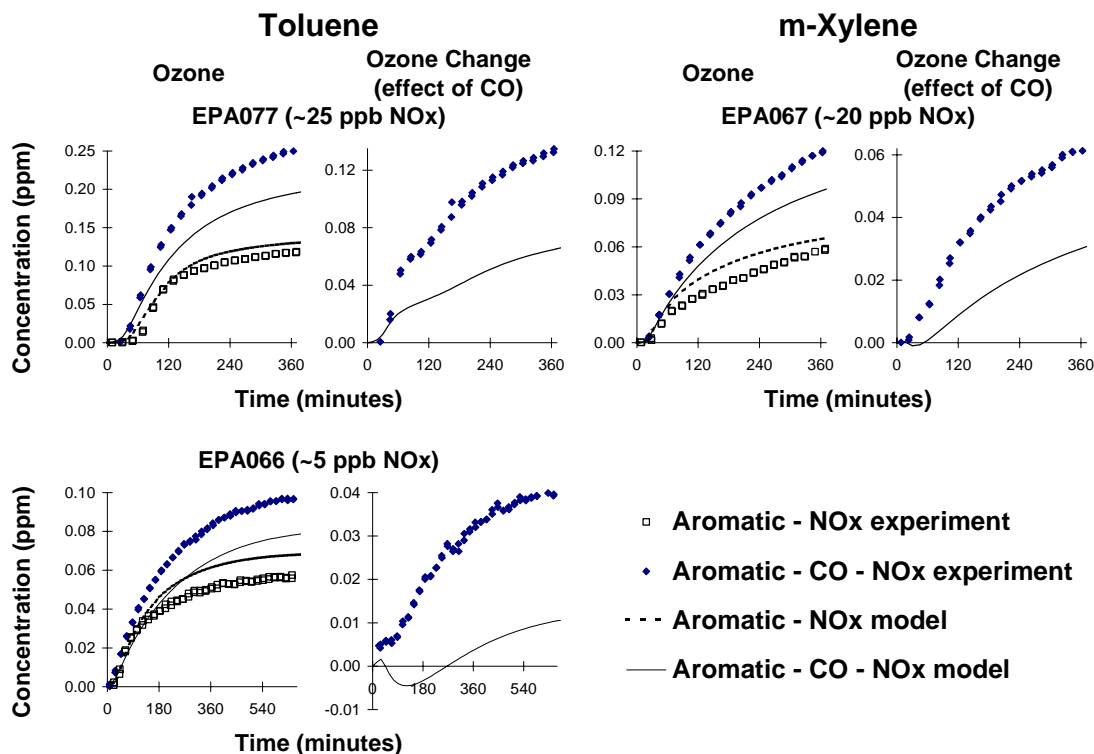


Figure 5. Experimental and calculated effects of CO addition on selected aromatics - NO_x experiments carried out in the UCR EPA chamber

However, the new UCR EPA chamber dataset also includes experiments where the effect of adding CO to aromatics - NO_x irradiations was determined. These experiments were carried out because model calculations indicated that the addition of CO would cause a significant enhancement in O₃ formation, due to the NO to NO₂ conversions caused when CO reacts with the radicals produced in the aromatic photooxidation reactions, and we wanted to test this prediction. In this regard, CO acts as a “radical amplifier”, enhancing the effects of radicals on ozone formation. CO addition is also useful because CO has the simplest possible mechanism to represent other VOCs present in ambient mixtures; its reactions only cause NO to NO₂ conversions and its reactions result in formation of no other products or direct radical sources or sinks. Therefore, added CO experiments should provide a test of an aspect of the aromatics mechanisms that is applicable to its effects in ambient simulations, and that is different than the tests provided by aromatic NO_x experiments in the absence of other VOCs.

The results of the aromatics - NO_x experiments with the added CO were consistent with the model in that the added CO did indeed significantly increase ozone formation, but the amount of O₃ increase was about twice what the model predicted. This is shown on Figure 5, where the filled diamonds show the O₃ in the aromatic - NO_x experiments or the change in O₃ caused by adding the CO, and the solid lines show the corresponding model predictions. About the same underprediction of the CO addition effect is seen for m-xylene as toluene, but the underprediction may be greater in the lower NO_x toluene experiment.

The underprediction of the effect of the added CO suggests that the mechanism is underpredicting the radical input in the aromatic photooxidation process. The fact that the same mechanism can simulate O₃ formation in the aromatics - NO_x experiments without the CO indicates that there probably are compensating errors in the mechanism. Further evidence for this comes from the fact that the mechanism *overpredicts* NO to NO₂ conversions in “direct reactivity” aromatic + HONO experiments that are much more sensitive to NO to NO₂ conversions in the mechanisms than radical sources (Carter and Malkina, 2002), suggesting that there may be too many NO to NO₂ conversions in the aromatics mechanisms.

However, reducing the NO to NO₂ conversions in the SAPRC-99 aromatics mechanism to fit the direct reactivity data and re-adjusting the radical input parameters to simulate the aromatics - NO_x experiments does not fully correct this problem. This is shown on Figure 6, which shows the model predictions of effects of CO, direct reactivity, and O₃ formation in toluene - NO_x runs with the standard and modified SAPRC-99 toluene mechanisms. Although the modified mechanism predicts an increase in O₃ caused by the added CO compared to the standard mechanism, the increase is insufficient. Even increasing the radical input in the to levels that result in overprediction of O₃ in the toluene - NO_x experiments is still not sufficient for the model to simulate the full effect of the CO addition.

Thus the new data suggest that there is a fundamental problem with the formulation of the current aromatics mechanism, and more extensive modifications are required in order for model simulations to be consistent with the available data. We have been funded by the California Air Resources Board to update the SAPRC mechanism, and developing an improved aromatics mechanism is a priority in this project. Work on a new, more explicit mechanism that incorporates more recent laboratory data such as that summarized by Calvert et al (2004) is now underway, but progress is slow. Presently, we are encountering problems similar to those

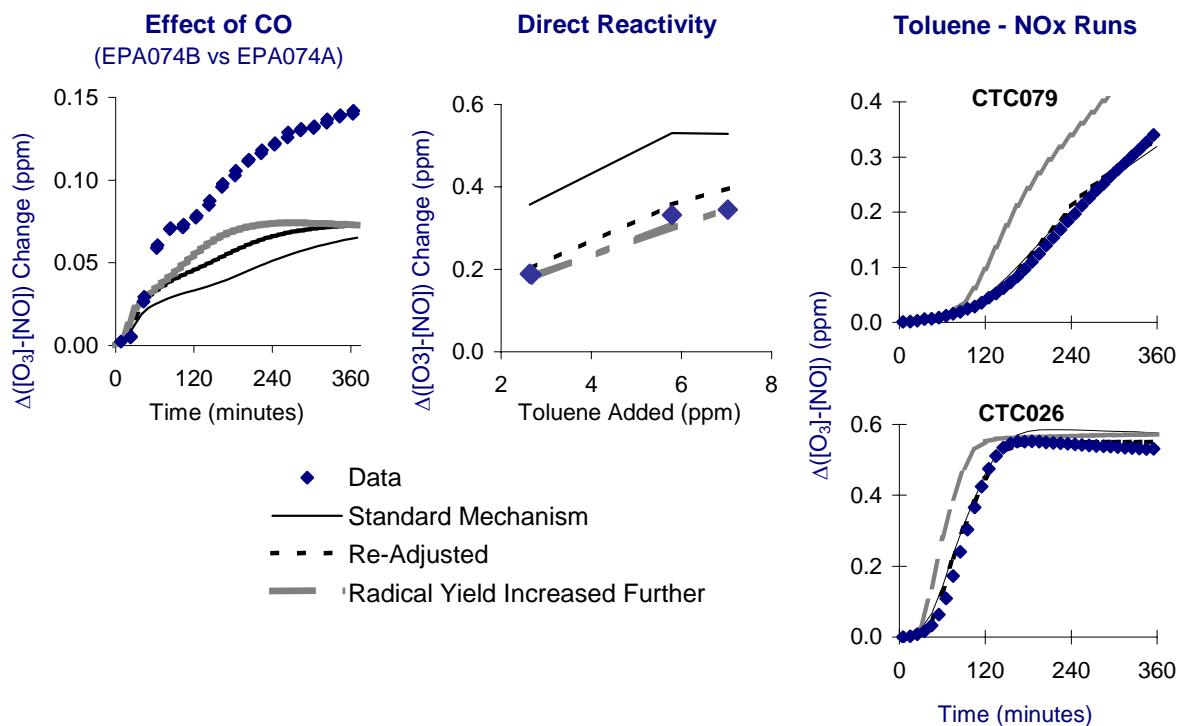


Figure 6. Effects of adjustments to the SAPRC-99 toluene photooxidation mechanism on simulations of representative toluene experiments experiments.

discussed by Pilling (2004) for the MCM. It is likely that there are reactions occurring that none of the mechanisms are adequately representing.

Conclusions

Although the UCR EPA chamber has only been in operation for a relatively short time, it has already obtained useful information concerning the performance of current mechanism in predicting the effects of VOCs and NO_x on ozone formation. As discussed here and also in our companion paper (Carter, 2004a), the SAPRC-99 mechanism predicts O₃ formation reasonably well in low NO_x experiments, and in ambient simulation experiments at the high ROG/NO_x levels where maximum ozone formation potentials are achieved. However, the new data indicate problems with the mechanisms that were not previously realized. The SAPRC-99 mechanism consistently underpredicts O₃ formation in the lower ROG/NO_x experiments where O₃ formation is most sensitive to VOCs, and the problem is even worse for CB4. Other experiments indicate that there are problems with the formulation with the current aromatics photooxidation mechanisms. It is possible that the problems with the underprediction at low ROG/NO_x ratios may be caused by problems with the aromatics mechanisms. Experimental and mechanism development work to investigate and hopefully resolve these problems is underway

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